

WO 00/53687

PCT/EP00/01931

**Sol-gel coating for single-coat or multicoat paint
systems**

0914545-083001
FOOEEB" 54547660

The present invention relates to a novel sol-gel
5 coating material for producing sol-gel coatings atop
single-coat or multicoat paint systems. The present
invention relates in particular to a novel process for
producing coated substrates, especially coated
automobile bodies, by initially providing the
10 substrates with a multicoat paint system and then
applying a sol-gel coating material thereatop and
curing it.

Automobile bodies are for the most part provided with a
15 multicoat coating system. As the final coat, it is
common to apply clearcoat materials. Useful clearcoat
materials include the customary and known one
component, two component, multicomponent (three
component, four component) powder or powder slurry
20 clearcoat materials or UV curable clearcoat materials.

One component, two component or multicomponent (three
component, four component) clearcoat materials are
described for example in the patent documents
25 US-A-5,474,811, US-A-5,356,669, US-A-5,605,965,
WO 94/10211, WO 94/10212, WO 94/10213, EP-A-0 594 068,
EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
WO 94/222969, EP-A-0 596 460 or WO 92/22615.

Powder clearcoat materials are known for example from German patent document DE-A-42 22 194 or BSF Lacke + Farben AG's 1990 Pulverlacke product bulletin.

- 5 Powder slurry coatings are powder coatings in the form of aqueous dispersions. Slurries of this kind are described for example in the US patent US-A-4,268,542 and the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 and the German patent application
10 DE-A-198 14 471.7, which was unpublished at the priority date of the present invention.

- UV curable clearcoat materials are disclosed for example in the patent documents EP-A-0 540 884,
15 EP-A-0 568 967 or US-A-4,675,234.

- Each of these clearcoat materials has specific strengths and weaknesses. They do provide multicoat paint systems meeting the optical requirements. Yet the
20 mar-resistant one component clearcoat materials are occasionally not sufficiently weathering resistant, whereas the weathering resistant two component or multicomponent (three component, four component) clearcoat materials are frequently insufficiently mar
25 resistant. Some one component clearcoat materials are mar resistant and stable to weathering, but combined with frequently employed waterborne basecoat materials give rise to surface defects such as wrinkling.

0944545-083001

Powder clearcoat materials, powder slurry clearcoat materials and UV curable clearcoat materials, by contrast, possess an unsatisfactory intercoat adhesion without wishing to imply that the mar resistance or
5 etch resistance problems are completely solved.

Recently, materials known as sol-gel clearcoats and based on siloxane-containing coating formulations have been developed which are obtained by hydrolysis and
10 condensation of silane compounds. These coating materials, which are used as coating compositions on plastics, are described for example in the German patent documents DE-A-43 03 570, 34 07 087, 40 11 045, 40 25 215, 38 28 098, 40 20 316 or 41 22 743.

15 Sol-gel clearcoats impart very good mar resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This mar resistance is not achieved by the known OEM (original
20 equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automotive industry is now demanding that this improved mar resistance be transferred to the clearcoat materials used in the finishing of automobiles as well.

25 Replacing the OEM clearcoat materials or OEM powder slurry clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials is not a straightforward matter, however, since the sol-gel

00014545-083001
100000-5454560

These problems can be solved by curing the clearcoat which is to be coated with the sol-gel clearcoat only partially, so that the sol-gel coat can be chemically anchored as it were on the clearcoat in the course of the conjoint curing. However, this approach would require that, on one and the same coating line, the clearcoats on automobile bodies which are to be overcoated have to be cured at a different temperature than the clearcoats of the other automobile bodies which are not to be overcoated. The use of different curing conditions on one and the same coating line constitutes a substantial disadvantage. This disadvantage is additionally aggravated by the fact that the second layer of clearcoat material requires a long oven drying time to cure.

.

novel sol-gel coating material whereby the advantageous properties of the sol-gel coatings are combinable with the advantageous properties of the known single-coat or multicoat paint systems, especially the multicoat paint systems for automotive OEM coating, without any need for departures from the customarily employed coating process, especially the wet on wet process of automotive OEM coating. In other words, the novel sol-gel coating material shall permit the subsequent application, within a short time, of a mar resistant coating atop ready produced, previously cured paint systems without any adhesion problems arising in the process.

This object is achieved by the novel sol-gel coating material comprising

(A) an acrylate copolymer solution comprising at least one acrylate copolymer (A1) preparable by copolymerizing at least the following monomers:

- a1) at least one (meth)acrylic ester which is substantially free of acid groups,
- a2) at least one ethylenically unsaturated monomer which bears at least one hydroxyl group per molecule and is substantially free of acid groups, and

a3) at least one ethylenically unsaturated monomer which bears per molecule at least one acid group which is convertible to the corresponding acid anion group;

5

(B) a free stock coating material preparable by hydrolyzing and condensing at least one hydrolyzable silane (B1) of the general formula I

10

SiR_4 (I)

where the variable R has the following meaning:

15

R = hydrolyzable groups, hydroxyl groups and nonhydrolyzable groups with the proviso that there is at least one and there are preferably at least two hydrolyzable group(s);

20 and

(C) a sol preparable by hydrolyzing, condensing and complexing at least one hydrolyzable silane (B1) of the general formula I and at least one hydrolyzable metal compound (C1) of the general formula II

25

MR_n (II)

100E80-5454T660

where the variables and the index have the following meaning:

M = aluminum, titanium or zirconium,

5

R = hydrolyzable groups, hydroxyl groups and nonhydrolyzable groups with the proviso that there is at least one and there are preferably at least two hydrolyzable group(s), and

10

n = 3 or 4.

In what follows, the novel sol-gel coating material will be referred to as the subject coating material.

15

The present invention also provides the novel process for producing sol-gel coatings on single-coat or multicoat paint systems by

20

(i) applying a single-coat or multicoat paint system to a primed or unprimed substrate,

(ii) applying a sol-gel coating material atop the single-coat or multicoat paint system and

25

(iii) curing the sol-gel coating material,

characterized in that a subject coating material is used.

TOP SECRET

In what follows, the novel process for producing sol-gel coatings atop single-coat or multicoat paint systems will be referred to as the subject process for brevity.

5

The invention further provides novel sol-gel coatings which are preparable from the subject coating materials and will hereinafter be referred to as the subject sol-gel coatings.

10

Not least the invention provides novel substrates which comprise at least one subject sol-gel coating and will hereinafter be referred to as the subject substrates.

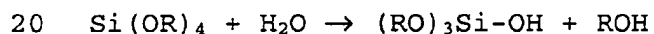
- 15 In the light of the background art, it is surprising and unforeseeable for one skilled in the art that the object underlying the invention is accomplished by the subject coating material and the subject process. It is especially surprising that the subject coating material
- 20 should readily adhere to the ready produced, cured paint systems without detachments or cracks occurring on stone chipping or following exposure to condensation, i.e., ten days' exposure of the coats in an atmosphere of 40°C and 100% relative humidity.
- 25 Moreover, the optical properties of the paint systems provided with the subject sol-gel coatings meet all requirements.

The subject coating material is a siloxane-containing

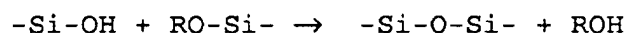
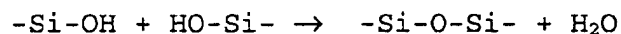
09914545-083001
TO0000-5454T660

- coating formulation which can be prepared by reacting hydrolyzable silicon compounds with water or water-detaching agents and which contains organic constituents to improve certain properties. A general
- 5 description of such systems may be found for example in the article by Bruce M. Novak, "Hybrid Nanocomposite Materials - Between Inorganic Glasses and Organic Polymers", in Advanced Materials, 1993, 5, No. 6, pages 422-433, or in the contribution of R. Kasemann,
- 10 H. Schmidt to the 15th International Conference, International Centre for Coatings Technology, Paper 7, "Coatings for mechanical and chemical protection based on organic-inorganic Sol-Gel Nanocomposites", 1993.
- 15 The basic reactions take place in a sol-gel process in which tetraorthosilicates are hydrolyzed and condensed in the presence or absence of a cosolvent:

Hydrolysis:



Condensation:



25

in which R may be alkyl, such as methyl or ethyl. Tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) are frequently used. The reactions are catalyzed using acids, bases or fluoride ions.

09014545 082001
T00230" 5454T660

The subject coating material accordingly comprises siloxane-containing structures modified by organic constituents (Ormocer® = Organically Modified Ceramic).

5 The subject sol-gel coating is produced by controlled hydrolysis and condensation of silicate esters and of metal alkoxides. Specific properties are conferred on the subject sol-gel coating through the incorporation into the silicatic network of organically modified
10 silica derivatives. They allow the construction of an organic polymer network in addition to the basic inorganic scaffold when organic radicals are used which preferably contain olefinically unsaturated groups and/or epoxide groups.

15 The modifying can be effected for example by having a ready produced organic polymer present during the hydrolysis and condensation of the starting materials or in the sol.

20 The subject coating material consists of the three essential components (A), (B) and (C).

Component (A) is an acrylate polymer solution. It is
25 preferably free of aromatic solvents.

For the purposes of the present invention, the expression "free of aromatic solvents" or "aromatics free" is to be understood here and hereinbelow as

00914545 "082001
100280" 5454T660

meaning that the level of aromatic solvents or aromatic compounds in a solution is <1 weight %, preferably <0.5 weight % and particularly preferably <0.2 weight % and is especially below the limit of detection by gas chromatography.

09014545-083001
100000-STAT-60

The acrylate polymer solution (A) to be used according to the invention contains at least one acrylate copolymer (A1) which is prepared by a copolymerization of the hereinbelow specified monomers (a1), (a2) and (a3) and optionally further monomers (a4), (a5) and/or (a6) wherein (a1), (a2) and (a3) and also optionally (a4), (a5) and (a6) are chosen in terms of type and amount in such a way that the acrylate copolymer (A1) has the desired OH number, acid number and molecular weight. The acrylate polymers (A1) preferably have a hydroxyl number of 40 to 240, particularly preferably 60 to 210 and especially 100 to 200, an acid number of 5 to 100, particularly preferably 10 to 60 and especially 20 to 40, glass transition temperatures of -35 to +85°C and number average molecular weights Mn of 1 000 to 300 000.

The polyacrylate resins used inventively may be prepared using as monomer (a1) any (meth)acrylic acid alkyl or cycloalkyl ester which is copolymerizable with (a2), (a3), (a4), (a5) and (a6) and has up to 20 carbon atoms in the alkyl radical, especially methyl, ethyl, propyl, n-butyl, sec-butyl, tert-butyl, hexyl,

ethylhexyl, stearyl and lauryl acrylate or meth-
acrylate; cycloaliphatic (meth)acrylates, especially
cyclohexyl, isobornyl, dicyclopentadienyl, octahydro-
4,7-methano-1H-indenemethanol or tert-butylcyclohexyl
5 (meth)acrylate; (meth)acrylic oxaalkyl or oxacycloalkyl
esters such as ethyltriglycol (meth)acrylate and
methoxyoligoglycol (meth)acrylate having a molecular
weight Mn of preferably 550; or other ethoxylated
and/or propoxylated, hydroxyl-free (meth)acrylic acid
10 derivatives. These monomers may include, in minor
amounts, more highly functional (meth)acrylic alkyl or
cycloalkyl esters such as ethylene glycol, propylene
glycol, diethylene glycol, dipropylene glycol, butylene
glycol, 1,5-pentanediol, 1,6-hexanediol, octahydro-4,7-
15 methano-1H-indenedimethanol or 1,2-, 1,3- or 1,4-
cyclohexanediol di(meth)acrylate; trimethylolpropane
di- or tri(meth)acrylate; or pentaerythritol di-, tri-
or tetra(meth)acrylate. In the context of the present
invention, minor amounts of higher-functional monomers
20 are those amounts that do not lead to crosslinking or
gelling of the polyacrylate resins.

As the monomer (a2) it is possible to use any
ethylenically unsaturated monomers which are
25 copolymerizable with (a1), (a2), (a3), (a4), (a5) and
(a6) and different from (a5) which carry at least one
hydroxyl group per molecule and are substantially free
of acid groups, such as hydroxyalkyl esters of acrylic
acid, methacrylic acid or another alpha,beta-ethyl-

09514545-083001
T00280-54547660

enically unsaturated carboxylic acid which is derived from an alkylene glycol which is esterified with the acid or are obtainable by reacting the acid with an alkylene oxide; especially hydroxyalkyl esters of

5 acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl

10 acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, mono-

15 maleate, monofumarate or monoitaconate; or reaction products of cyclic esters, such as epsilon-caprolactone, for example, and these hydroxyalkyl esters; or olefinically unsaturated alcohols such as allyl alcohol or polyols such as trimethylolpropane

20 monoallyl or diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether. As far as these higher-functional monomers (a2) are concerned, the comments made for the higher-functional monomers (a1) apply analogously. The proportion of trimethylolpropane

25 monoallyl ether is usually from 2 to 10 weight %, based on the overall weight of the monomers (a1) to (a6) used to prepare the polyacrylate resin. In addition, however, it is also possible to add from 2 to 10% by weight, based on the overall weight of the monomers

09514545.033001

used to prepare the polyacrylate resin, of trimethylolpropane monoallyl ether to the finished polyacrylate resin. The olefinically unsaturated polyols, such as trimethylolpropane monoallyl ether in particular, may be used as sole hydroxyl-containing monomers, but in particular may be used proportionately in combination with other of the abovementioned hydroxyl-containing monomers.

- 10 As the monomer (a3) it is possible to use any ethylenically unsaturated monomer, or mixture of such monomers, which carries at least one acid group, preferably one carboxyl group, per molecule and is copolymerizable with (a1), (a2), (a4), (a5) and (a6).
- 15 As component (a3) it is particularly preferred to use acrylic acid and/or methacrylic acid. However, other ethylenically unsaturated carboxylic acids having up to 6 carbon atoms in the molecule may also be used. Examples of such acids are ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid. It is further possible to use ethylenically unsaturated sulfonic or phosphonic acids, and/or their partial esters, as component (a3). Further suitable components (a3) include mono(meth)acryloyloxyethyl maleate,
- 25 succinate and phthalate.

As the monomer (a4) it is possible to use one or more vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule. The

000000-000000

00914545-083004
T0020-54545-083004

branched monocarboxylic acids may be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence of a liquid, strongly acidic catalyst; the olefins may be cracking products of paraffinic hydrocarbons, such as mineral oil fractions, and may comprise branched and straight-chain acyclic and/or cycloaliphatic olefins. The reaction of such olefins with formic acid or with carbon monoxide and water produces a mixture of carboxylic acids in which the carboxyl groups are located predominantly on a quaternary carbon atom. Other olefinic starting materials are, for example, propylene trimer, propylene tetramer and diisobutylene. Alternatively, the vinyl esters may be prepared in a conventional manner from the acids; for example, by reacting the acid with acetylene. Particular preference, owing to their ready availability, is given to the use of vinyl esters of saturated aliphatic monocarboxylic acids having 9 to 11 carbon atoms which are branched on the alpha carbon atom.

As the monomer (a5), use is made of the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule. Glycidyl esters of highly branched monocarboxylic acids are available under the trade name "Cardura". The reaction of the acrylic or methacrylic acid with the glycidyl ester of a carboxylic acid having a tertiary alpha

carbon atom can take place before, during or after the polymerization reaction. As the component (a5) it is preferred to use the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of
5 Versatic acid. This glycidyl ester is commercially available under the name "Cardura E10".

As the monomer (a6) it is possible to use all ethylenically unsaturated monomers, or mixtures of such
10 monomers, which are copolymerizable with (a1), (a2), (a3), (a4) and (a5), are different from (a1), (a2), (a3) and (a4), and are substantially free from acid groups. Suitable components (a6) include the following:

15 - olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, cyclohexene, cyclopentene, norbornene, butadiene, isoprene, cyclopentadiene and/or dicyclopentadiene;

20 - (meth)acrylamides such as (meth)acrylamide, N-methyl-, N,N-dimethyl-, N-ethyl-, N,N-diethyl-, N-propyl-, N,N-dipropyl-, N-butyl-, N,N-dibutyl-, N-cyclohexyl- and/or N,N-cyclohexylmethyl(meth)-acrylamide;

25 - monomers containing epoxide groups, such as the glycidyl ester of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid and/or itaconic acid;

09014545-083001
T00280" STAT 660

- vinylaromatic hydrocarbons, such as styrene, alpha-alkylstyrenes, especially alpha-methylstyrene, and/or vinyltoluene;
- 5 - nitriles such as acrylonitrile and/or methacrylonitrile;
- vinyl compounds such as vinyl chloride, vinyl fluoride, vinylidene dichloride, vinylidene difluoride; N-vinylpyrrolidone; vinyl ethers such as ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether and/or vinyl cyclohexyl ether; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate and/or the vinyl ester of 2-methyl-2-ethylheptanoic acid; and/or
- 10 - polysiloxane macromonomers having a number-average molecular weight Mn of from 1 000 to 40 000, preferably from 2 000 to 20 000, with particular preference from 2 500 to 10 000 and in particular from 3 000 to 7 000 and having on average from 0.5 to 2.5, preferably from 0.5 to 1.5, ethylenically unsaturated double bonds per molecule, as described in DE-A-38 07 571 on pages 5 to 7, in DE-A-37 06 095 in columns 3 to 7, in EP-B-0 358 153 on pages 3 to 6, in US-A-4,754,014 in columns 5 to 9, in DE-A-44 21 823 or in the
- 20
- 25

09014545-083001

international patent application WO 92/22615 on
page 12, line 18 to page 18, line 10, or
acryloxysilane-containing vinyl monomers,
preparable by reacting hydroxy-functional silanes
5 with epichlorohydrin and subsequently reacting the
reaction product with methacrylic acid and/or
hydroxyalkyl esters of (meth)acrylic acid.

Preference is given to using vinylaromatic
10 hydrocarbons, especially styrene.

The nature and amount of the monomers (a1) to (a6) is
selected such that the polyacrylate resin (A1) has the
desired OH number, acid number, and glass transition
15 temperature. Acrylate resins used with particular
preference are obtained by polymerizing

(a1) from 20 to 60% by weight, preferably from 30 to
50% by weight, of the component (a1),

20

(a2) from 0 to 50% by weight, preferably from 0 to 40%
by weight, of the component (a2),

(a3) from 1 to 15% by weight, preferably from 1 to 8%
25 by weight, of the component (a3),

(a4) from 0 to 25% by weight of the component (a4),

(a5) from 0 to 25% by weight of the component (a5), and

09445-08300
T00C80-5454F660

(a6) from 5 to 30% by weight, preferably from 10 to 20%
by weight, of the component (a6),

the sum of the weight fractions of the components (a1)
5 to (a6) being 100% in each case.

The inventively employed acrylate copolymers (A1) are
prepared in an organic solvent or solvent mixture,
which is preferably free of aromatic solvents, and in
10 the presence of at least one polymerization initiator.
Polymerization initiators used are the polymerization
initiators which are customary for the preparation of
acrylate copolymers.

15 Examples of suitable polymerization initiators are
initiators which form free radicals, such as, for
example, tert-butyl peroxyethylhexanoate, benzoyl
peroxide, di-tert-amyl peroxide, azobisisobutyro-
nitrile, and tert-butyl perbenzoate. The initiators are
20 used preferably in an amount of from 1 to 25% by
weight, with particular preference from 2 to 10% by
weight, based on the overall weight of the monomers.

The polymerization is advantageously conducted at a
25 temperature of from 80 to 200°C, preferably from 110 to
180°C.

Preferred solvents used are ethoxyethyl propionate and
isopropoxypropanol.

09044545-083004
FOOESQ-S454T660

The acrylate copolymer (A1) is preferably prepared by a two-stage process since the resulting subject coating materials have a better processability. Preferred acrylate copolymers (A1) are therefore obtainable by

5

1. polymerizing a mixture of the monomers (a1) and (a2) and, if desired, (a4), (a5) and/or (a6), or a mixture of portions of the monomers (a1) and (a2) and also, if desired, (a4), (a5) and/or (a6), in an organic solvent, and

10

2. after at least 60% by weight of the mixture of (a1) and (a2) and, if desired, (a4), (a5) and/or (a6) have been added, adding the monomer (a3) and any remainder of the monomers (a1) and (a2) and, if appropriate, (a4), (a5) and/or (a6), and continuing polymerization.

15

In addition, however, it is also possible to include the monomers (a4) and/or (a5) in the initial charge, together with at least some of the solvent, and to meter in the remaining monomers. Furthermore, it is also possible for only some of the monomers (a4) and/or (a5) to be included in the initial charge, together with at least some of the solvent, and for the remainder of these monomers to be added as described above. Preferably, for example, at least 20% by weight of the solvent and about 10% by weight of the monomers (a4) and (a5), and, if desired, portions of the

20

25

0941515-083001
FOUO 80-51515-083001

monomers (a1) and (a6), are included in the initial charge.

Preference is further given to a two-stage process for the preparation of the inventively used acrylate polymers (A1) in which the first stage lasts for from 1 to 8 hours, preferably from 1.5 to 4 hours, and the mixture of (a3) and any remainder of the monomers (a1), (a2) and, if appropriate, (a4), (a5) and (a6) is added over the course of from 20 to 120 minutes, preferably over the course of from 30 to 90 minutes. Following the end of the addition of the mixture of (a3) and any remainder of the monomers (a1) and (a2) and, if appropriate, (a4), (a5) and (a6) polymerization is continued until all of the monomers used have undergone substantially complete reaction. In this case, the second stage may follow on immediately from the first. Alternatively, the second stage may be commenced only after a certain time, for example, after from 10 minutes to 10 hours.

The amount, and rate of addition, of the initiator is preferably chosen so as to give an acrylate copolymer (A1) having a number-average molecular weight M_n of from 1 000 to 30 000 daltons. It is preferred to commence the addition of initiator some time, generally from about 1 to 15 minutes, before the addition of the monomers. Furthermore, preference is given to a process in which the addition of initiator is commenced at the

00014545-003001

15 Preferably, the monomers for preparing the acrylate copolymers (A1) are polymerized with not too high a polymerization solids, preferably with a polymerization solids of from 80 to 50% by weight, based on the monomers, and then the solvents are partially removed by distillation, so that the resulting acrylate copolymer solutions (A1) have a solids content of preferably from 100 to 60% by weight.

25 For use in the subject coating material, the solids content of the acrylate copolymer solutions (A1) is adjusted with at least one aromatics-free solvent to less than 60% by weight, preferably less than 40% by weight, and in particular less than 30% by weight.

The preparation of the acrylate copolymers (A1) for
5 inventive use has no special features in terms of
method but instead takes place with the aid of the
methods which are customary and known in the field of
polymers for continuous or batchwise copolymerization
under atmospheric or superatmospheric pressure in
10 stirred vessels, autoclaves, tube reactors or Taylor
reactors.

In accordance with the invention, Taylor reactors are advantageous.

20 Taylor reactors, which serve to convert substances under the conditions of Taylor vortex flow, are known. They consist essentially of two coaxial concentric cylinders of which the outer is fixed while the inner
25 rotates. The reaction space is the volume formed by the gap between the cylinders. Increasing angular velocity ω_i of the inner cylinder is accompanied by a series of different flow patterns which are characterized by a dimensionless parameter, known as the Taylor number Ta .

As well as the angular velocity of the stirrer, the Taylor number is also dependent on the kinematic viscosity ν of the fluid in the gap and on the geometric parameters, the external radius of the inner cylinder r_i , the internal radius of the outer cylinder r_o and the gap width d , the difference between the two radii, in accordance with the following formula:

$$Ta = \omega_i r_i d \nu^{-1} (d/r_i)^{1/2} \quad (I)$$

where $d = r_o - r_i$.

At low angular viscosity, the laminar Couette flow, a simple shear flow, develops. If the rotary speed of the inner cylinder is increased further, then, above a critical level, alternately contrarotating vortices (rotating in opposition) occur, with axes along the peripheral direction. These vortices, called Taylor vortices, are rotationally symmetric and have a diameter which is approximately the same size as the gap width. Two adjacent vortices form a vortex pair or a vortex cell.

The basis of this behavior is the fact that, in the course of rotation of the inner cylinder with the outer cylinder at rest, the fluid particles that are near to the inner cylinder are subject to a greater centrifugal force than those at a greater distance from the inner cylinder. This difference in the acting centrifugal forces displaces the fluid particles from the inner to

00000-5454T660

5

10

20

25

5 The proportion of the constituent (A) in the subject coating material may vary very widely and is guided in particular by the intended flexibility of the subject sol-gel coating produced therefrom. There is an upper limit on the proportion; thus, it may not be chosen so high that phase separation occurs in the subject coating material, or the hardness and mar resistance of the sol-gel coating decrease too sharply. The skilled worker is therefore able to determine the proportion which is optimal in each case, on the basis of his or her knowledge in the art, with or without the assistance of simple preliminary tests.

It is produced by controlled hydrolysis and condensation of at least one organically modified hydrolyzable silane (B1). It is of advantage according to the invention to use at least two silanes (B1).

The hydrolyzable silane (B1) comprises compounds of the general formula I

SiR_n (I)

where the R radicals can be identical or different and are selected from hydrolyzable groups, hydroxyl groups
5 and nonhydrolyzable groups.

The nonhydrolyzable groups R in the general formula I are preferably selected from alkyl groups, especially of 1 to 4 carbon atoms, for example methyl, ethyl,
10 propyl and butyl groups; alkenyl groups, especially of 2 to 4 carbon atoms, for example vinyl, 1-propenyl, 2-propenyl and butenyl groups; alkynyl groups, especially of 2 to 4 carbon atoms such as acetylenyl and propargyl groups; and aryl groups, especially of 6
15 to 10 carbon atoms, for example phenyl and naphthyl groups. Nonhydrolyzable groups R used are preferably alkyl groups.

Examples of hydrolyzable groups R in the aforementioned
20 formula I are hydrogen atoms; alkoxy groups, especially of 1 to 20 carbon atoms, for example methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, tert-butoxy and sec-butoxy groups; alkoxy-substituted alkoxy groups, for example beta-methoxyethoxy groups; acyloxy groups,
25 especially of 1 to 4 carbon atoms, for example acetoxy and propionyloxy groups; and alkylcarbonyl groups such as for example acetyl groups.

Particularly preferred hydrolyzable groups R are those

00914545-083001
T00000"SHS4T660

which bear no substituents and lead to aromatics-free hydrolysis products having a low molecular weight, for example lower alcohols, such as methanol, ethanol, propanol, n-butanol, i-butanol, sec-butanol and
5 tert-butanol.

At least one group R of the formula I shall be a hydrolyzable group. Silanes (B1) with two, preferably four and especially three hydrolyzable groups R are
10 particularly preferred.

The nonhydrolyzable groups R of the silanes (B1) may contain at least one functional group. These functional groups may be for example epoxide groups, amino groups,
15 olefinically unsaturated groups such as vinyl or (meth)acryloyl groups, mercapto groups, isocyanate groups and/or their reaction products with further reactive compounds.

20 Examples of hydrolyzable silanes (B1) particularly useful for the purposes of the invention are methyltriethoxysilane, methyltrimethoxysilane, tetramethyl orthosilicate, tetraethyl orthosilicate, 3-glycidyloxypropyltrimethoxysilane or 3-aminopropyl-
25 triethoxysilane.

The silanes (B1) can be used in whole or in part in the form of precondensates, i.e., compounds formed by partial hydrolysis of the silanes (B1), either alone or

09914545.00000
FOOEBD.5454T660

The hydrolysis and condensation may optionally be carried out in the presence of organic monomers, of solvents, preferably aromatics-free solvents, of the hereinbelow described organically modified hydrolyzable metal alkoxides (C1) and of metal oxides in the form of nanoparticles.

20 in the absence of an organic solvent.

In a further variant, the hydrolysis and condensation of the hydrolyzable silanes (B1) is carried out in the presence of an aromatics-free organic solvent, such as an aliphatic alcohol, such as methanol, ethanol, propanol, isopropanol or butanol, an ether, such as dimethoxyethane, an ester such as dimethylglycol acetate or methoxypropyl acetate and/or 2-ethoxyethanol or a ketone such as acetone or methyl ethyl ketone.

5

10

15

25

Similarly, the fraction of the subject coating material which is attributable to the constituent (B) can vary within very wide limits and depends in particular on

the target mar resistance and hardness for the subject sol-gel coating produced therefrom. The fraction has an upper limit; it must not be so high as to cause phase separation in the subject coating material and/or excessive hardness and brittleness for the subject sol-gel coatings produced therewith. The skilled worker is therefore able to determine the best fraction in each case on the basis of his or her expertise with or without the assistance of simple preliminary tests.

10

The further essential constituent of the subject coating material is the sol (C), which is preparable by hydrolysis, condensation and complexation of at least one of the hereinabove described silanes (B1) and at least one hydrolyzable metal compound (C1) of the general formula II. The sol (C) is preferably aromatics-free.

In the general formula II, the variable M is aluminum, titanium or zirconium, but especially aluminum. Accordingly, the index n is 3 or 4.

In the general formula II, the variable R has the same meaning as specified hereinabove in the case of the general formula I. According to the invention, it is of advantage here for at least two, especially three hydrolyzable groups to be present in the case of aluminum and three, especially four, in the case of titanium or zirconium.

According to the invention, the hereinabove described alkoxy groups are particularly advantageous and are therefore preferred. Very particular preference is given to sec-butyloxy groups. An example of a very
5 particularly preferred hydrolyzable metal compound (C) is accordingly aluminum tri-sec-butoxide.

The molar ratio of metal M to silicon can vary within very wide limits and depends in particular on the
10 target mar resistance of the subject sol-gel coatings. Generally, replacing a portion of the silicon with aluminum in particular will enhance the mar resistance and the hardness of the subject sol-gel coatings. More particularly, the molar ratio M:Si is in the range from
15 1:10 to 1:1.5, preferably in the range from 1:6 to 1:3.

The hereinabove described silanes (B1) and metal compounds (C1) are hydrolyzed and condensed according to the invention in the presence of at least one
20 organic, preferably nonaromatic, compound capable of forming chelate ligands. Concerned are organic compounds having at least two functional groups capable of coordinating onto metal atoms or ions. These functional groups are customarily electron donors which
25 offer up electrons to metal atoms or ions as electron acceptors. According to the invention, in principle all organic compounds of the type mentioned are suitable, provided they do not adversely affect or even completely prevent the hydrolysis and condensation

0914545-083001

and/or the crosslinking to the ready produced sol-gel coating. Examples of suitable organic compounds are compounds containing carbonyl groups in the 1,3 position, such as acetylacetone or ethyl acetate.

5

The hydrolysis, condensation and complexation is effected substantially under the conditions specified hereinabove for the production of the stock coating material (B). More particularly, the silanes (B1),
10 metal compounds (C1) and the organic compounds capable of forming chelates are initially charged, whereupon the mixture is admixed, preferably at lower temperatures, especially 0°C, with water and at least one of the hereinabove described condensation
15 catalysts. The reaction can be carried out in the presence of the hereinabove described solvents and/or nanoparticles. According to the invention, however, it is of advantage for the reaction to be carried out in the absence of these components. Since the resulting
20 sol (C) is very reactive, it is advisable to keep it at temperatures below 0°C until it is to be put to further use.

The fraction of the subject coating material which is
25 attributable to the constituent (C) can likewise vary within very wide limits and depends in particular on how the performance profile with regard to mar resistance and hardness on the one hand and flexibility on the other is to be balanced out for the subject sol-

00000-545460

5

15

20

25

—

—

The subject coating material may further contain an additive solution (D). It is preferably aromatics-free.

5 The additive solution (D) contains at least one ethylenically unsaturated compound (d1) which has at least one epoxide group. An example of a suitable compound (d1) is glycidyl (meth)acrylate.

10 It further contains as component (d2) at least one silane (B1) having at least one nonhydrolyzable group R which contains at least one epoxide group. An example of a suitable compound (d2) is 3-glycidyloxypropyltrimethoxysilane.

15 Not least, it contains at least one adduct (d3) of at least one silane (B1) with at least one nonhydrolyzable group R which has at least one amino group and with at least one cyclic ethylenically unsaturated dicarboxylic anhydride. An example of a suitable silane (B1) is 3-aminopropyltriethoxysilane. Examples of suitable
20 dicarboxylic anhydrides are maleic anhydride and itaconic anhydride.

The additive solution contains the components (d1), (d2) and (d3) in a weight ratio of (1 to 10):(1 to
25 30):1, especially (2 to 6):(10 to 20):1. The solids content of the additive solution (D) is preferably below 80 weight %, preferably below 60 weight % and especially below 50 weight %.

30 The fraction of the subject coating material which is

1000000 5454560

attributable to the additive solution (D) can vary within wide limits, if the additive solution (D) is used. The skilled worker can determine whichever is the best fraction on the basis of his or her expertise with or without the assistance of simple preliminary tests.

The subject coating material can further contain major amounts of solvents, preferably aromatics-free solvents, as constituent (E). This is the case especially which particularly thin subject sol-gel coatings, preferably having a dry film thickness $<5 \mu\text{m}$, are to be produced. Examples of suitable solvents (E) are the hereinabove mentioned lower alcohols, especially ethanol, or glycol ethers such as ethylglycol or butylglycol.

The subject coating material can further contain customary known coating additives (F). All coating additives (F) are suitable which do not adversely affect, but advantageously vary and improve the properties profile of the subject sol-gel coatings, especially their optical properties (appearance) and mar resistance.

Examples of suitable coating additives (F) are

- UV absorbers;
- free radical scavengers;

09914545-083001
T00280-5454T660

- catalyts for crosslinking;
- slip additives;
- 5 - polymerization inhibitors;
- defoamers;
- antipopping agents, in regard to which the
10 controlled use of minor amounts of aromatic
solvents may be of benefit;
- emulsifiers, especially nonionic emulsifiers such
as alkoxyated alkanols and polyols, phenols and
alkylphenols or anionic emulsifiers such as alkali
15 metal salts or ammonium salts of alkanecarboxylic
acids, alkanesulfonic acids and sulfonic acids of
alkoxyated alkanols and polyols, phenols and
alkylphenols;
- 20 - wetting agents such as siloxanes, fluorous
compounds, carboxylic monoesters, phosphoric
esters, polyacrylic acids and their copolymers or
polyurethanes;
- 25 - adhesion promoters;
- flow control agents;
- film-forming auxiliaries such as cellulose

00914545.0830001
T00E80" S4S4T660

derivatives;

- flame retardants or

- 5 - rheology control additives such as those known
from the patent documents WO 94/22968,
EP-A-0 276 501, EP-A-0 249 201 or WO 97/12945;
crosslinked polymeric microparticles, as disclosed
for example in EP-A-0 008 127; inorganic
10 phyllosilicates such as aluminum-magnesium
silicates, sodium-magnesium and sodium-magnesium-
fluorine-lithium phyllosilicates of the
montmorillonite type; silicas such as Aerosils; or
synthetic polymers having ionic and/or associative
15 groups such as polyvinyl alcohol, poly(meth)-
acrylamide, poly(meth)acrylic acid, polyvinyl-
pyrrolidone, styrene-maleic anhydride or ethylene-
maleic anhydride copolymers and their derivatives
or hydrophobic modified ethoxylated urethanes or
20 polyacrylates.

Further examples of suitable coating additives (F) are
described in the textbook Lackadditive by Johan
Bieleman, Wiley-VCH, Weinheim, New York, 1998.

25

The subject coating material has a solids content of up
to 80, preferably up to 60, particularly preferably up
to 40 and especially up to 20 weight %. When
particularly thin subject sol-gel coatings, i.e.

00044545-083004

coatings <5 μm in thickness, are to be produced, it is advisable to select a solids content of less than 20% by weight.

- 5 The production of the subject coating material has no particular features, but is effected in conventional and known manner by mixing its essential constituents (A), (B) and (C) and also optionally (D), (E) and/or (F) in customary and known mixing assemblies such as
- 10 dissolvers. The constituents can be mixed with each other in any desired manner. For example, they can be introduced into the mixing assembly all at once. According to the invention, however, it is advantageous to initially charge the sol (C) and then to add the
- 15 remaining constituents one by one in succession. It is advantageous in this process to add the stock coating material (B) before the acrylate copolymer solution (A). When a solvent (E) is used, it is advantageously added after the addition of the stock coating solution
- 20 (B) and before the addition of the constituent (A) and optionally (D). When coating additives (F) are used, they are advantageously added after the addition of the stock coating solution (B) and before the addition of the constituent (A). When solvents (E) and coating
- 25 additives (F) are used, the coating additives (F) are added before the addition of the solvents (E).

The subject coating materials are very useful for producing the subject sol-gel coatings, especially sol-

09914545.083001
T000280.91817660

According to the invention, any conceivable substrate can be coated therewith. By way of example, mention may

case of plastic, the priming may take the form of hydropriming. In the case of metal, the substrate may

methods such as spraying, knife coating, spread coating, casting, dipping or rolling can be used.

be preceded by a predrying step. Again the customary and known processes and apparatuses such as through air

possible to specifically coat and make mar resistant
only parts of substrates or single-coat or multicoat

stress. This enables the subject coating materials to be used in automotive repair finishing. Since here, moreover, the amount of the subject coating material can be restricted to a minimum, its use is also particularly economical.

The subject coating materials can be applied directly to the substrates in order that a mar resistant subject sol-gel coating may be formed thereon after curing. In this way it is possible to obtain mar resistant finishes on substrates as are customary for the manufacture of vehicles, of other structural parts and equipment, such as radiators or containers, or of furniture.

However, the particular advantages of the subject coating materials become particularly evident when they are used for coating single-coat or multicoat paint systems with the subject sol-gel coatings. It proves to be a particular advantage here that the single-coat or multicoat paint systems may have been completely cured.

Accordingly, the subject coating materials are useful for coating single-coat or multicoat paint systems of the type customary and known in the fields of automotive original equipment manufacturing coatings, automotive repair coatings, industrial coatings, including container coatings, plastics coatings and furniture coatings.

0944545-083001

Examples of single-coat paint systems of this kind are the solid shade topcoats known in automotive original equipment manufacturing finishing, which contain binders, crosslinkers and effect- and/or color-
5 conferring pigments.

Examples of multicoat paint systems are those which contain an effect- and/or color-conferring basecoat, especially a waterborne basecoat, and a clearcoat and
10 are generated in the realm of automotive original equipment manufacturing coating by the wet on wet process as described for example in the patent documents US-A-3,639,147, DE-A-33 33 072, DE-A-
38 14 853, GB-A-2 012 191, US-A-3,953,644,
15 EP-A-0 260 447, DE-A-39 03 804, EP-A-0 320 552,
DE-A-36 28 124, US-A-4,719,132, EP-A-0 297 576,
EP-A-0 069 936, EP-A-0 089 497, EP-A-0 195 931,
EP-A-0 228 003, EP-A-0 038 127 and DE-A-28 18 100, or
in the realm of automotive repair finishing. The
20 subject coating materials are particularly useful for coating multicoat paint systems of this kind in particular.

Examples of suitable waterborne basecoats and of
25 corresponding multicoat paint systems are known from the patent documents EP-A-0 089 497, EP-A-0 256 540,
EP-A-0 260 447, EP-A-0 297 576, WO 96/12747,
EP-A-0 523 610, EP-A-0 228 003, EP-A-0 397 806,
EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211,

05914545 083001
FOOEEB" SHST650

- EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092,
EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484,
EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817,
WO 95/14721, EP-A-0 521 928, EP-A-0 522 420,
5 EP-A-0 522 419, EP-A-0 649 865, EP-A-0 536 712,
EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818,
EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536,
EP-A-0 354 261, EP-A-0 424 705, WO 97/49745,
WO 97/49747 or EP-A-0 401 565.
- 10 Examples of suitable one component, two component or
multicomponent (three component, four component)
clearcoat materials are known for example from the
patent documents DE-A-42 04 518, US-A-5,474,811,
US-A-5,356,669, US-A-5,605,965, WO 94/10211,
15 WO 94/10212, WO 94/10213, EP-A-0 594 068,
EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
WO 94/22969, EP-A-0 596 460 or WO 92/22615.

One component clearcoat materials, as will be known,
20 contain hydroxyl-containing binders and crosslinkers
such as blocked polyisocyanates, tris(alkoxycarbonyl-
amino)triazines and/or aminoplast resins. In a further
variant they contain polymers having pendant carbamate
and/or allophanate groups as binders and optionally
25 carbamate- and/or allophanate-modified aminoplast
resins as crosslinkers.

Two-component or multicomponent (three component, four
component) clearcoat materials, as will be known,

000145-083001
FOOEO-SAT660

contain hydroxyl-containing binders and polyisocyanate crosslinkers as essential constituents, which have to be kept separated before use.

5 Examples of suitable powder clearcoat materials are known for example from the German patent document DE-A-42 22 194 or BASF Lacke + Farben AG's 1990 Pulverlacke product information bulletin.

10 Powder clearcoat materials, as will be known, contain epoxy-containing binders and polycarboxylic acid crosslinkers as essential constituents.

15 Examples of suitable powder slurry clearcoat materials are known from the US patent US-A-4,268,542 and the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 or are described in the German patent application DE-A-198 14 471.7, which was unpublished at the priority date of the present invention.

20 Powder slurry clearcoat materials, as will be known, contain powder clearcoat materials dispersed in an aqueous medium.

25 UV curable clearcoat materials are disclosed for example in the patent documents EP-A-0 540 884, EP-A-0 568 967 or US-A-4,675,234.

As will be known, they contain actinically and/or

09014545-083001
FOUO-90-54545-083001

electron beam curable low molecular weight, oligomeric and/or polymeric compounds, preferably radiation curable binders, especially on the basis of ethylenically unsaturated prepolymers and/or ethylenically unsaturated oligomers, optionally one or more reactive diluents and also optionally one or more photoinitiators. Examples of suitable radiation curable binders are (meth)acryloyl-functional (meth)acryloyl copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates and the corresponding methacrylates. Preference is given to using binders which are free of aromatic structural units.

15

However, it is also possible to employ multicoat clearcoat systems such as for example a clearcoat system based on hydroxyl-containing binders and blocked polyisocyanates and aminoplasts as crosslinkers, which is situated directly atop the waterborne basecoat and on top of which there is a further clearcoat based on carbamate and/or allophanate group containing binders and aminoplasts as crosslinkers.

25 In the subject process, the single-coat or multicoat paint systems, especially the clearcoats, are cured prior to application of the subject coating material. This constitutes a further particular advantage of the subject coating material and of the process, since the coating processes and apparatuses customarily used in

commercial practice do not have to be modified; all that is needed is that a customary known process is followed by a further coating step which is essentially independent thereof.

5

It proves to be a further particular advantage that substantially all customarily used clearcoat systems can be coated with the subject coating material.

- 10 The subject sol-gel coatings which are produced from the subject coating materials, preferably by the subject process, are notable for excellent mar resistance coupled with very good adhesion, even after exposure to condensation. Similarly, the appearance is
- 15 very good. The subject process is therefore particularly useful for the coating of vehicle bodies, especially automobile bodies, with multicoat systems; for industrial coating, including coil coatings, plastics coating and furniture coating.

20

Examples

Preparation Example

- 25 **Preparation of subject sol-gel clearcoat material**

1. Preparation of a stock coating material

- 30 parts of completely ion-free water, 40 parts of
- 30 ethylglycol, 5 parts of acetic acid (100%), 66.5 parts

099454E-083001
FOUOED-5454E660

of methyltriethoxysilane and 4.7 parts of 3-glycidyl-
oxypropyltrimethoxysilane were charged under nitrogen
to a suitable reaction vessel and heated to 60°C with
stirring. Following a further 3 hours at 60°C, the
5 stirred reaction mixture was heated to 90°C and
maintained at 90°C for 2 hours. 70 parts of the
reaction mixture were then distilled off azeotropically
at 85°C. After cooling to room temperature, the
reaction mixture was admixed with 5 parts of
10 methoxypropyl acetate and 0.1 part of BYK® 301 (flow
control agent from BYK). The result was stock coating
material 1 having a theoretical solids content of 37%
by weight and an experimentally determined solids
content of 45% by weight (1 hour/130°C).

15

**2. Preparation of an acrylate copolymer for modifying
the sol-gel clearcoat material**

39 parts of ethoxyethyl propionate were charged to a
20 suitable stirred vessel equipped with reflux condenser
and stirrer and were heated to 130°C. A first monomer
feed vessel was used to premix 9.598 parts of butyl
methacrylate, 7.708 parts of methyl methacrylate,
8.003 parts of styrene, 4.253 parts of Methacrylester
25 13.0 (methacrylic ester having a long alkyl radical in
the ester moiety) and 9.096 parts of hydroxyethyl
acrylate. A second monomer feed vessel was charged with
3.810 parts of hydroxyethyl acrylate, 1.831 parts of
acrylic acid and 0.916 part of ethoxyethyl propionate.

0914545-083001
FO0E80-5454T660

09014545-0830001
T00030-5454T660

An initiator feed vessel was charged with 3.692 parts of TBPEH (tert-butyl perethylhexanoate) peroxide and 6.025 parts of ethoxyethyl propionate. The contents of the first monomer feed vessel were metered into the reactor at a uniform rate over four hours. After two hours and 30 minutes after the start of the first monomer feed, the second monomer feed was started. To this end, the contents of the second monomer feed were metered into the reactor at a uniform rate over one hour and 30 minutes. The contents of the initiator feed vessel were metered into the reactor at a uniform rate over four hours and 30 minutes, the start of the initiator feed being started five minutes before the first monomer feed. After the additions, the resulting reaction mixture was polymerized at 130°C for two hours until an original viscosity of 2.2 dPas, a solids content of 50% by weight (15 minutes/180°C) and an acid number of 30 mg of KOH/g have been obtained. Thereafter, the ethoxyethyl propionate was distilled off at 100°C under reduced pressure until a solids content of 81% by weight was reached. The resulting reaction mixture was cooled to 80°C and adjusted to a solids content of 75% by weight with butylglycol and ethoxyethyl propionate (weight ratio 5:1).

25

To prepare the subject sol-gel clearcoat material, the solution of the acrylate copolymer was adjusted to a solids content of 20% by weight with butylglycol to obtain the solution for the organic modification 2.

3. Preparation of a sol to be used according to the invention

FOOEEB" SHET 660

A mixture of 138.6 parts of aluminum tri-sec-butoxide, 5 178.3 parts of methyltriethoxysilane, 401.78 parts of 3-glycidyloxypropyltrimethoxysilane and 82.6 parts of ethyl acetate was charged to a suitable reaction vessel at 0°C. 198.72 parts of 0.1 N hydrochloric acid were metered into the initial charge at 0°C. After addition, 10 the resulting reaction mixture was aged at room temperature for 24 hours. Assuming 100% conversion, the theoretical solids content was 37.88% by weight and the theoretical solvent content 53.11% by weight. The experimentally determined solids content was 44.6% by 15 weight (15 minutes/180°C). The pH of the Ormocer solution was 3.1. The viscosity (original) was 20 mPas at a shear gradient $D = 103 \text{ s}^{-1}$. The sol was kept at -18°C until used for preparing the subject sol-gel clearcoat material.

20

4. Preparation of the subject sol-gel clearcoat material

The sol-gel clearcoat material 4 was obtained by 25 initially charging 9.81 parts of the sol 3 and adding to it in succession 35.8 parts of the stock coating material 1 (45% by weight in ethylglycol), 0.2 parts of BYK® 301, 65 parts of ethanol and 40 parts of the solution for organic modification 2 with stirring and

mixing the constituents. The result was the subject sol-gel clearcoat material 4 having a solids content of 19% by weight.

5 Example

1. Preparation of a subject sol-gel coating on a multicoat paint system

- 10 A commercially available surfacer from BASF Coatings AG was applied with a cup gun to steel panels cathodically coated to a depth of 18-22 μm with a commercially available electrocoat material and baked in. The result was a surfacer coat 35 to 40 μm in thickness. A
- 15 commercially available black solid shade basecoat material from BASF Coatings AG was then applied atop the surfacer in the same way and predried at 80°C for 10 min. After cooling the panels, a coat of a commercially available two component clearcoat material
- 20 (FF98-0015 from BASF Coatings AG) was applied and predried at 50°C for 10 min and then crosslinked at 140°C together with the basecoat for 45 min. The result was a basecoat 15 μm in thickness and a clearcoat 44 μm in thickness. The black solid shade basecoat material
- 25 was chosen because any marring is most easily detectable on the corresponding test panels.

After cooling, the subject sol-gel clearcoat material 4 of the preparation example was applied, so that the

00014545 003001
FOUO 30 54 66

subject sol-gel coating was obtained in a thickness of 4.5 μm after curing with intermediate IR radiation (distance of radiator from surface 18 cm; radiator: Modul Infrarotstrahler MMS 2000 from Haraeus).

5

2. Testing of the properties of the subject sol-gel coating

2.1 Adhesion of the sol-gel coating

10

Table 1 gives an overview of the mechanical tests and of the results obtained.

Table 1:

15

Adhesion of subject sol-gel coating

Test methods	Example
Mar test DBL 7399 [rated from 0 to 5]	0
Mar test after 240 hours of constant condensation conditions (CCC) [rated from 0 to 5]	0
Cross-hatch to DIN 53151 (2 mm) [rated from 0 to 5]	0

09041515-033001
F00080" 5151760

Cross-hatch after 240 hours of CCC and
24 hours of regeneration 0

[rated from 0 to 5]; 0 = best value; 5 = worst value

Although the clearcoat had been completely baked prior
5 to its overcoating with the sol-gel coating, there was
no delamination of the sol-gel coating.

2.2 Mar resistance of the sol-gel coating by the brush test

10

Before this test was carried out, the test panels were
aged at room temperature for at least 2 weeks following
application of the coatings.

15 The mar resistance of the sol-gel coating on the test
panels was assessed with the aid of the BASF brush test
described in Fig. 2 on page 28 of the article by
P. Betz and A. Bartelt, Progress in Organic Coatings,
22 (1993), pages 27 -37, albeit with modification with
20 regard to the weight used (2 000 g instead of the 280 g
mentioned therein), assessment taking place as follows:

In the test, the surface of the paintwork was damaged
with a mesh fabric loaded with a mass. The mesh fabric
25 and the paintwork surface were copiously wetted with a
laundry detergent solution. The test panel was moved to

00914515-083001
FOUOESD-5454T660

and fro underneath the mesh fabric in reciprocal movements by means of a motor drive.

Test element was an eraser (4.5 × 2.0 cm, broad side
5 perpendicular to the direction of marring) covered with
nylon mesh fabric (No. 11, 31 μm mesh size, Tg 50°C).
The applied weight was 2 000 g.

Prior to each test, the mesh fabric was renewed, with
10 the running direction of the fabric meshes parallel to
the direction of marring. Using a pipette, about 1 ml
of a freshly stirred 0.25% strength Persil solution was
applied in front of the eraser. The rotary speed of the
motor was adjusted so that 80 double strokes were
15 performed within a period of 80 s. After the test, the
remaining wash liquor was rinsed off with cold tap
water and the test panel was blown dry with compressed
air.

20 It was found that the subject sol-gel coatings were
completely free of any marring.

2. Surface slip of subject sol-gel coating

25 The surface slip was measured using the MOD 9505AE -
SERIAL 7035-0689-2 slip meter from ALTEK, P.O. Box
1128, Torrington, Connecticut 06790, USA. In this
measurement, a weight provided with three hemispheres
was pulled with a constant force over the surface of

0914545 083001
100500 54547660

the test panels. The frictional resistance which occurred when this done was plotted graphically as a dimensionless variable using an x/y plotter. The height of the resultant peak is a relative measure of the lubricity of the surface in question: the lower the height, the more lubricious the surface.

In this test, the sol-gel coating had a relative peak height of 0.06. For comparison, the commercially customary two component clearcoat material (FF98-0015 from BASF Coatings AG) used to produce the multicoat system had a relative peak height of 0.05.

2.4 Chemical resistance

2.4.1 Chemical resistance by the MB gradient oven test

In the well-known MB gradient oven test, the test panels of the example were exposed under defined condition to damage by sulfuric acid, water, pancreatin and tree resin. For this purpose, the test substances were applied at a distance of one segment width in each case (adjustment of the gradient to 30 - 75°C [1°C per heating segment]). Following storage under standard conditions 23°C for 72 hours, the test panels were exposed for 30 min in a gradient oven (e.g. type 2615 from BYK-Gardner). The temperature at which the first visible change occurred was determined.

The experimental results are reported in Table 2.

00914515-063001
T00290" 5154T660

Table 2: Chemical resistance by the MB gradient oven test

Test substance	Example
	1st marking at °C
Sulfuric acid 1%	54
Water distilled	>75
Pancreatin	48
Tree resin	>75

- 5 The results of the MB gradient oven test substantiate the high chemical resistance of the subject sol-gel coating.

2.4.2 Resistance to dishwasher detergent

10

This test was carried out using a dishwasher detergent having a pH of 10.8. The test panels were exposed to the amounts of detergent reported in Table 3, in the reported concentrations, at 23°C (conditioning cabinet) or 30°C (through air oven) for 30 minutes. The resulting damage was in each case rated as follows:

15

Rating Meaning

	0	no damage
	1	slight discoloration
5	2	discoloration
	3	edge marking

Table 3 gives an overview of the results obtained.

**Table 3: Resistance of subject sol-gel coating to
dishwasher detergent**

Amount of detergent (ml)	Temperature (°C)	Concentration	
		1%	5%
0.025	23	0	0
0.8025	30	1	1
0.05	30	0	0
0.075	30	0	0
0.1	30	0	0
0.125	30	0	0

The values of Table 3 substantiate the high chemical stability of the subject sol-gel coating.

FOOEBB" SHSTT660

2.5 Stone chipping test

AUDI AG's well-known stonechip test under multiple impact (2x500 gram/2 bar) yielded an index of 3 and a degree of rusting of 2. The subject sol-gel coating together with the multicoat paint system accordingly proved to be sufficiently stable to stone chipping.

2.6 Erichsen indentation

10

The Erichsen indentation to DIN EN ISO 1520: 1995-04 was 0.9 mm.

2.7 Appearance

15

2.7.1 Waviness

The waviness of the subject sol-gel coating was measured by wave scan. For this purpose, a laser beam was directed at the surface at an angle of 60° and the fluctuations of the reflected light were recorded over a stretch of 10 cm.

A value of 8.0 was found in the longwave range (0.6 to 10 mm; observer's distance: 2.5 m). There were accordingly no orange peel structures or other defects in the paintwork.

A value of 27.9 was found in the shortwave range (0.1

09914545.003001
T00000" sheet 60

to 0.6 mm; observer's distance: 45 cm). Accordingly, only few if any fine structures of this order of magnitude were present in the surface.

5 **2.7.2 Gloss and haze**

Gloss and haze were measured reflectometrically at an angle of 20° using a BYK reflectometer. The subject sol-gel coating had a gloss of 75 and a haze of 23 and
10 hence was in accord with commercial requirements in this respect as well.

09014545-083001
T00E90-5454T660